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An Investigation of Corrosion in Semiconductor Bridge Explosive Devices

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Abstract

In the course of a failure investigation, corrosion of the lands was occasionally found in developmental lots of semiconductor bridge (SCB) detonators and igniters. Evidence was found in both detonators and igniters of the gold layer being deposited on top of a corroded aluminum layer, but inspection of additional dies from the same wafer did not reveal any more corroded parts. In some detonators, evidence was found that corrosion of the aluminum layer also happened after the gold was deposited. Moisture and chloride must both be present for aluminum to corrode. A likely source for chloride is the adhesive used to bond the die to the header. Inspection of other SCB devices, both recently manufactured and manufactured about ten years ago, found no evidence for corrosion–even in devices that contained SCBs with aluminum lands and no gold. Several manufacturing defects were noted such as stains, gouges in the gold layer due to tooling, and porosity of the gold layer. Results of atmospheric corrosion experiments confirmed that devices with a porous gold layer over the aluminum layer are susceptible to extensive corrosion when both moisture and chlorine are present. The extent of corrosion depends on the level of chlorine contamination, and corrosion did not occur when only moisture was present. Elimination of the gold plating on the lands eliminated corrosion of the lands in these experiments. Some questions remain unanswered, but enough information was gathered to recommend changes to materials and procedures. A second lot of detonators was successfully built using aluminum SCBs, limiting the use of Ablebond™ adhesive, increasing the rigor in controlling exposure to moisture, and adding inspection steps.

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Materials

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Executive Summary

Corrosion of semiconductor bridge (SCB) dies was occasionally found during an FY05 failure investigation of developmental lots of detonators and igniters. These devices had a layer of gold deposited on top of aluminum lands. The corrosion of aluminum lands in the affected detonators was so severe that the gold layer delaminated. The aluminum layer of affected igniters was not as severely corroded. In these cases the corroded aluminum layer caused the gold layer to take on a rough appearance. The causes for failure of the detonators and igniters to function could not be blamed exclusively on corrosion, and the other failure mechanisms that were identified will be reported on separately. This report documents the corrosion aspects of the failure investigation. Corrosion is of concern, not only from an immediate failure standpoint, but also because these devices are intended to have a long life.

Focused ion beam cross sections of the corroded areas of both detonators and igniters indicated that the gold layer was deposited on corroded aluminum because the gold layer was of uniform thickness and intimately followed the rough topography of the corroded aluminum layer. Aluminum expands in volume as it corrodes, and so if the aluminum layer corroded after the deposition of the gold layer, one would expect to see areas where the gold layer had thinned or torn, but this was not the case. Nonetheless, all of the evidence is not consistent. Over a thousand SCB dies from the same wafer as that used to assemble the igniter were inspected, and no corroded parts were found. In some corroded detonators, it was clear that the aluminum layer also corroded after the gold was deposited because aluminum corrosion products were found on top of the gold layer.

Whether the aluminum corroded before or after the gold layer was deposited, analysis of the corroded area showed that chloride and moisture must have been present. The most likely source of chloride is the adhesive that was used to bond the die to the header and to support the wire bonds. A confirmed source of moisture could not be found, but because both lots of these devices were developmental, rigor in excluding moisture during manufacture did not have as high a priority as apparently is necessary. Both kinds of devices had been exposed to thermal cycling before function testing, but experiments showed that SCB devices are not inherently susceptible to corrosion upon thermal cycling only.

Because of the presence of corrosion in these two lots of SCB devices, samples of other SCB devices were also examined. Some groups had recently been manufactured and one group had been manufactured about ten years ago. The devices that were recently manufactured included a group of SCB detonators that did not contain a gold layer over the aluminum land. All of these devices were thermally cycled either as headers or fully assembled devices, and no evidence of corrosion was found.

Several manufacturing defects were observed in the devices with a gold layer on the aluminum lands. These included marks from a probe used to measure bridge resistance, gouges (probably from the wire bond tool), stains, and porosity in the gold layer. Gold is a soft metal that is easily deformed, and the marks and gouges often penetrated to the aluminum layer and sometimes to the polysilicon layer. Porosity was only noticed in recent dies, but no changes in process could be found to account for it. These observations are important because gold and aluminum form a galvanic couple, and aluminum will readily corrode where gold and aluminum are exposed to moisture and chloride. A solid gold layer may protect aluminum from corrosion, but a porous and compromised gold layer may well be worse from a corrosion standpoint than no gold layer at all. Some of the stains were attributed to thin layers of Ablebond™ adhesive that had wicked around the lands or to human skin oil and would be of concern for long term compatibility.

Atmospheric corrosion experiments were conducted using uncorroded igniter headers and exposure to a constant level of moisture and different concentrations of chlorine. The results were entirely consistent with what was expected. Extensive corrosion was found that initiated at sites where defects or pinholes in the gold exposed the underlying aluminum. As expected, the gold layer deformed and tore due to expansion of the aluminum layer as it corroded. Resistance measurements of the SCB showed that the resistance increased with time. With a

lower level of chlorine, the corrosion process took longer and was not as extensive. No corrosion and no rise in resistance values were noted when only moisture was present. Atmospheric corrosion experiments were also conducted with uncorroded detonator headers with aluminum lands. In these devices, no attack was seen on the aluminum lands or on the bond wires. The only attack was seen on the gold-plated posts (electrodes). The lack of observed corrosion was consistent with the SCB resistance measurements, which showed no increase over the duration of the exposure.

Based on the data collected and observations made in this investigation, several recommendations were made and incorporated into a second, successful lot of SCB detonators. The gold layer was eliminated which made the galvanic coupling concerns between the gold and the aluminum a moot point. Ablebond™ was used only to bond the die to the header. The chloride in the adhesive is not expected to be an issue if the adhesive is not used to support the wirebonds and if the amount of moisture present is minimized. Thus, rigor in minimizing moisture was increased to include drying steps, storage in dedicated desiccators, and a limit on the time a part could be out of desiccated storage. Finally, all headers were inspected, and any with dies that showed evidence of corrosion, stains, or other marks were discarded.

Introduction

The use of semiconductor bridge (SCB) technology in explosive components allows initiation of explosives with a relatively low amount of energy. These kinds of devices are attractive, therefore, in applications where available energy is limited. During FY05, failures to function were observed in a development lot of detonators and a development lot of igniters, and during the ensuing failure investigation, corrosion was found occasionally in both devices. The presence of corrosion is a concern from a failure standpoint, but the possibility of corrosion after deployment is also important because a long life is required for these devices. As it turned out, most of the failures to function could not be blamed on corrosion. The investigation also found evidence for other failure modes such as a detached bond wire and high density explosive powder. These failure mechanisms will be documented in a separate report. This report documents the corrosion aspects of the failure investigation.

Figure 1 illustrates a Type 3-2 SCB die, one of the more commonly used dies in explosive devices. The die contains a bowtie pattern of phosphorus-doped polysilicon on a silicon dioxide/ silicon substrate. An aluminum layer is added to both of the wide ends of the bowtie (lands) so that bond wires can be used to connect the lands to an external connector. In some devices a gold layer is deposited over the aluminum layer to protect it from the external environment. The narrow portion of the bowtie is the semiconductor bridge (SCB) and will burst upon application of the appropriate electrical energy, which in turn initiates the explosive. The bridge material is phosphorus-doped polysilicon and is not covered with aluminum. The bridge of a Type 3-2 SCB has a resistance of 1 ohm. In some devices Type 52 SCB dies are used, which have smaller bridges with a resistance of 2 ohms.

The development detonators were designed with a single Type 3-2 SCB die with one bridge whereas the igniters were designed with two Type 3-2 bridges (for redundancy) in a single die. Both kinds of dies had aluminum and gold layers that were applied using a thermal evaporation technique and that were approximately equal in thickness. When corrosion was found in the detonators, it was severe enough to cause delamination of large portions of the gold layer. When corrosion was present in the igniters, however, it was moderate and resulted in a rough surface appearance of the gold layer. No delamination was seen in any of the corroded igniters.

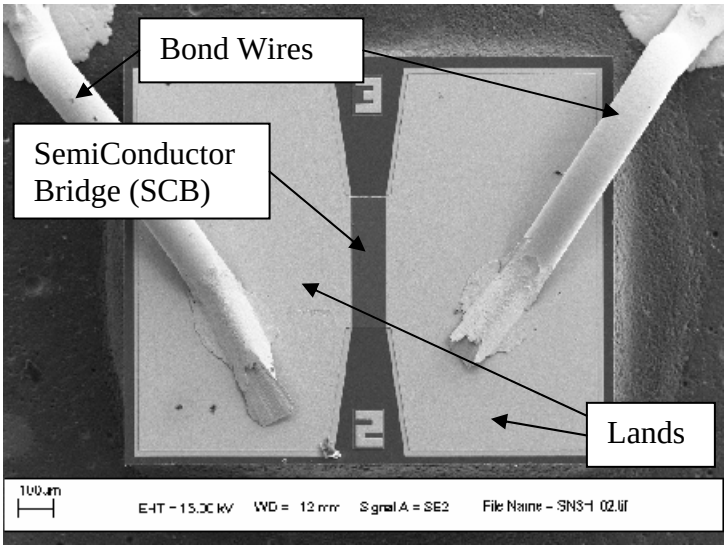

Figure 1. Example of a Type 3-2 SCB die.

Inspection and Analysis of Corroded Devices

Figure 2 shows a scanning electron micrograph of a focused ion beam (FIB) cut of an uncorroded land. The cross section shows the layers of polysilicon, aluminum, and gold as they should appear. Notice that the thicknesses of the gold and aluminum layers are approximately equal. The layers above the gold layer are platinum and gold/palladium layers that are applied during sample preparation. In comparison, Figure 3 shows a scanning electron micrograph of a FIB cut of a corroded land. The aluminum layer shows the swelling and cracking that is typical of corrosion due to the conversion of aluminum to aluminum corrosion products (hydrated oxy-chloride). The intimate contact of the gold layer with corroded aluminum along with the uniform thickness of the gold layer provides compelling evidence that gold was applied to corroded aluminum. If the aluminum layer had corroded after the gold layer was deposited, one would expect to see evidence for thinning or tearing of the gold layer as it was deformed by an expanding and corroding aluminum layer, and this was not observed in any of the corroded detonators or igniters.

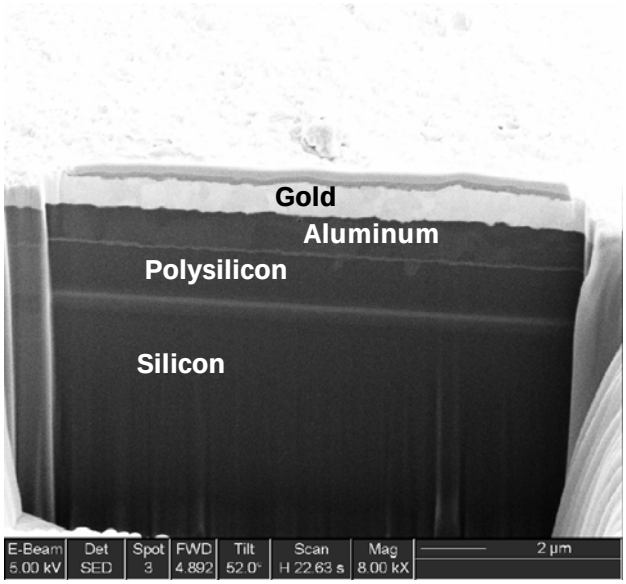

Figure 2. A FIB cut through an uncorroded land. The FIB cut shows a cross section of the aluminum, gold, and polysilicon layers.

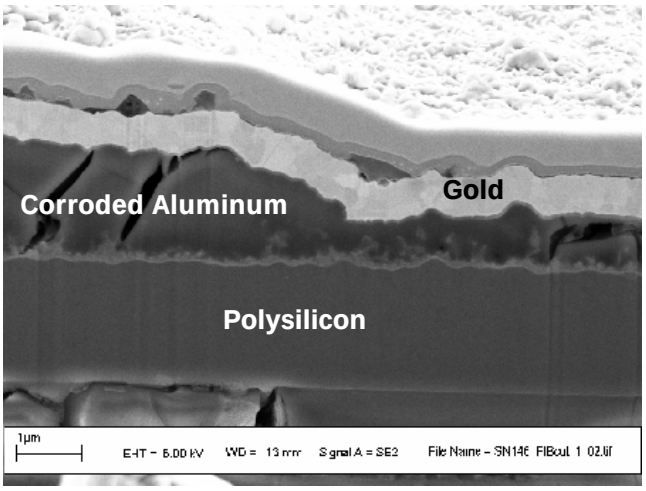

Figure 3. A FIB cut from the corroded land of an igniter.

Figure 4 shows FIB cuts from two different detonators that show the gold layer in direct contact with the polysilicon layer. In the figure on the left, there is no evidence of aluminum on top of the polysilicon. In the figure on the right, Al is present in part of the sample and is missing in other areas. Again, the intimate contact and uniform thickness suggests that the gold layer was deposited on an area where the aluminum was so corroded that areas of it were missing. The aluminum layer in the right hand micrograph shows areas where the aluminum is not corroded (left hand side), where it is corroded (middle), and where it is missing (right hand side). The gap between the gold and polysilicon layers at the right hand side of the figure is an artifact of sample preparation.

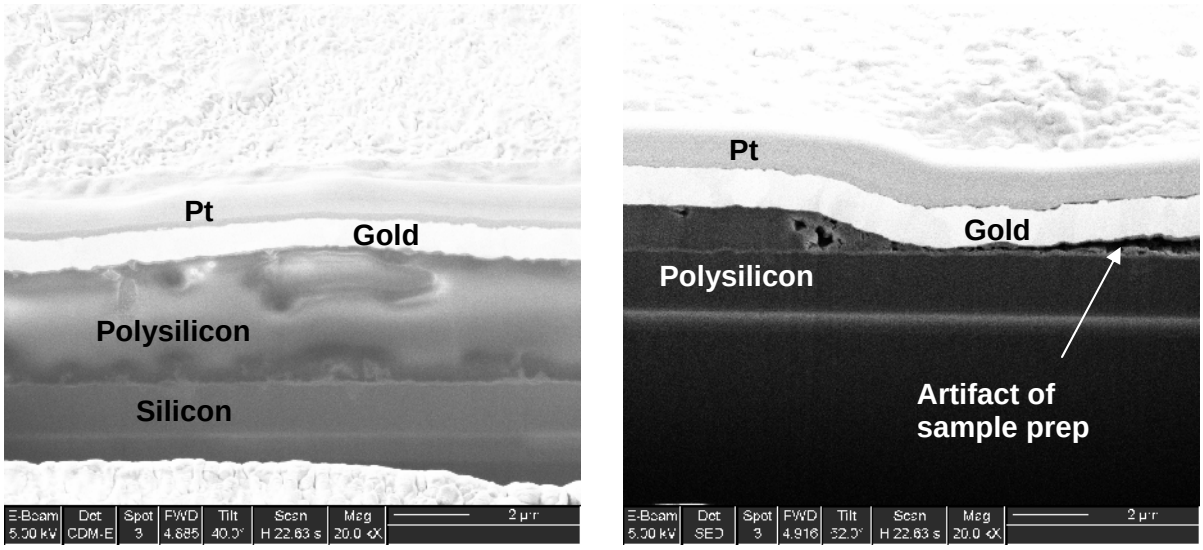

Figure 4. FIB cuts from detonators that show the gold layer in contact with the polysilicon layer.

In some of the detonators, it was evident that corrosion also took place after the gold was deposited because aluminum corrosion products were found on top of the gold layer. See, for example, the scanning electron micrograph in Figure 5 of a portion of a die. The mud-cracked material on top of the gold is made up of aluminum corrosion products that have dried, and implies that enough moisture was present at one time to allow transport of corrosion products over the surface of the die. Both the detonator and igniter are hermetic devices, and the mud-cracking most likely appeared after device disassembly exposed the corrosion products to air. Figure 6 shows the FIB cross section of a land from a detonator that looks similar to that in Figure 5, and corroded aluminum is found both above and below the gold layer.

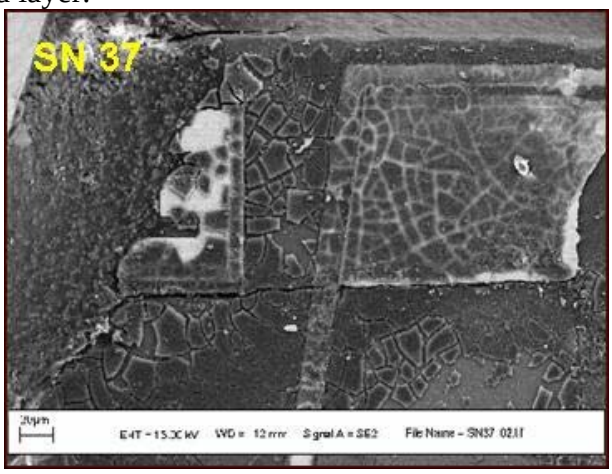

Figure 5. Top view of a detonator die that shows corrosion on the surface of the gold.

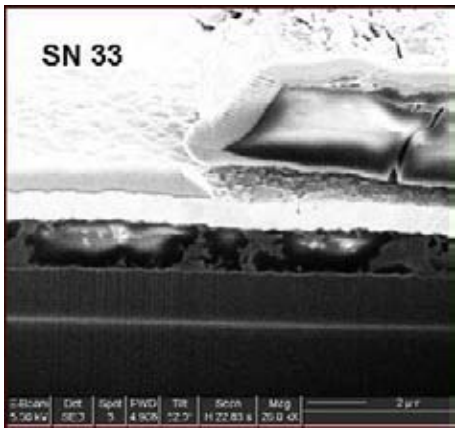

Figure 6. A FIB cut that shows corroded aluminum both above and below the gold layer.

Activities to Support the Corrosion Investigation

Because both of these devices were in the development stage, documentation of manufacturing and traceability of parts were not as rigorous as one would like to support an investigation of this kind. Anecdotal information was available, however, and enough data were gathered to make recommendations that allowed a successful build and lot acceptance test of a second developmental lot of detonators. A second lot of SCB igniters was not built because the design was changed to a hot wire bridge.

Several activities were pursued to understand the corrosion process and to determine its source, and these activities will be discussed in turn. If indeed, areas of the aluminum layer of a wafer were corroded before the gold layer was applied, then one should be able to find other dies from that same wafer that exhibit corrosion. It was not possible to trace the dies that were used in the detonator lot to particular wafers, but the dual SCB dies used for the igniter represented a unique design. Only one wafer had been made, and thus about 1,000 dies that had not been used in manufacturing igniters were available from this wafer for inspection. Experience with corroded parts showed that the rough surface texture of corroded lands was easily seen using an optical microscope. See, for example, the bottom two lands of Figure 7. Nonetheless, no corroded lands were found while inspecting over 1,000 dies.

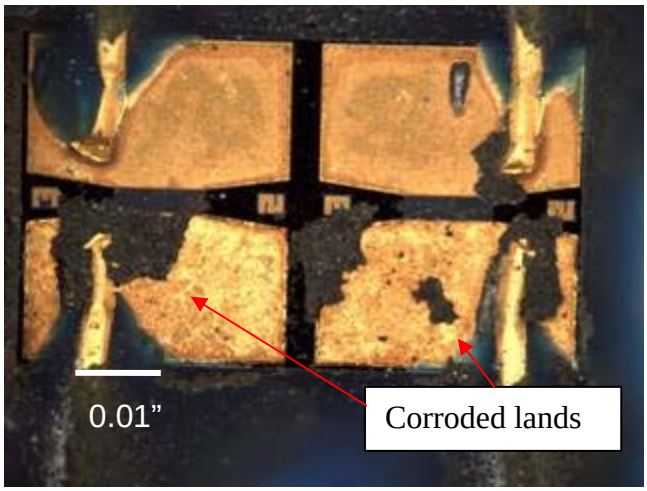

Figure 7. A dual Type 3-2 SCB from an igniter showing two corroded lands in close proximity to two uncorroded lands.

It was also observed that when corrosion was found in igniters, it was localized to anywhere from one to three lands of the die. For example, Figure 7 shows a dual SCB where the corrosion is localized to the bottom two lands. If random areas of corrosion existed on the wafer, one would not expect that for lands in such close proximity two would be corroded and the other two not. It is also improbable that if small areas of aluminum on the wafer were corroded before gold was deposited, only dies from those areas were used to manufacture the igniter. These inconsistencies with data that show the gold must have been deposited on corroded aluminum or areas where aluminum was missing remain unexplained.

As part of the lot qualification testing for both the detonators and the igniters, the devices were either thermally cycled (detonators)[1] or thermally shocked (igniters)[1] before function

[1] The detonators were thermally cycled for five cycles between -65°F (-54°C) and 160°F (71°C) and then 25 cycles between -40°F (-40°C) and 133°F(56°C). The thermal shock involved immediate exposure to a cold temperature of -80°F (-62°C) and then a hot temperature of 200°F (93°C) for five cycles with 20 minutes at each temperature extreme.

testing. Unfortunately, resistance measurements were not made immediately before thermal cycling—only after.[2] Thus, the question arose regarding the role of thermal cycling in corrosion processes. To determine if SCB devices were susceptible to corrosion upon thermal cycling two unloaded igniter headers and ten dual SCB dies were thermally shocked. In all cases the dies were free of corrosion before and after the thermal treatment indicating that the thermal cycling in and of itself did not contribute to corrosion.

The aluminum corrosion products, such as those seen on the corroded SCB dies, are related to the presence of both moisture and chloride. Aluminum will not corrode if one or the other is missing. The presence of moisture was inferred from the appearance of the corrosion products and knowledge of corrosion processes, but direct evidence for the presence of chlorine was obtained from Energy Dispersive X-Ray (EDS) analyses of the corroded areas of the dies. Several sources of chloride were considered, and Ablebond™ 968-2 was considered one of the most likely sources. Ablebond™ 968-2 was used as an adhesive to bond SCB dies to headers in both the detonator and igniter designs, and a fact sheet published by Ablestick Laboratories lists the chloride content of Ablebond™-968-2 as 215 ppm. Ablebond™ was also liberally applied to support the bond wires in both of these devices so that the wires would not deform from the pressure of loading the powder into the device. This practice, of course, places the adhesive in direct contact with the dies. An example is shown in Figure 8. It is common for the adhesive to wick around and onto the land and occasionally onto the bridge area. Fourier Transform Infrared (FTIR) spectroscopy was used to confirm that the material on the lands was, indeed, Ablebond™ adhesive but without the silica filler material.

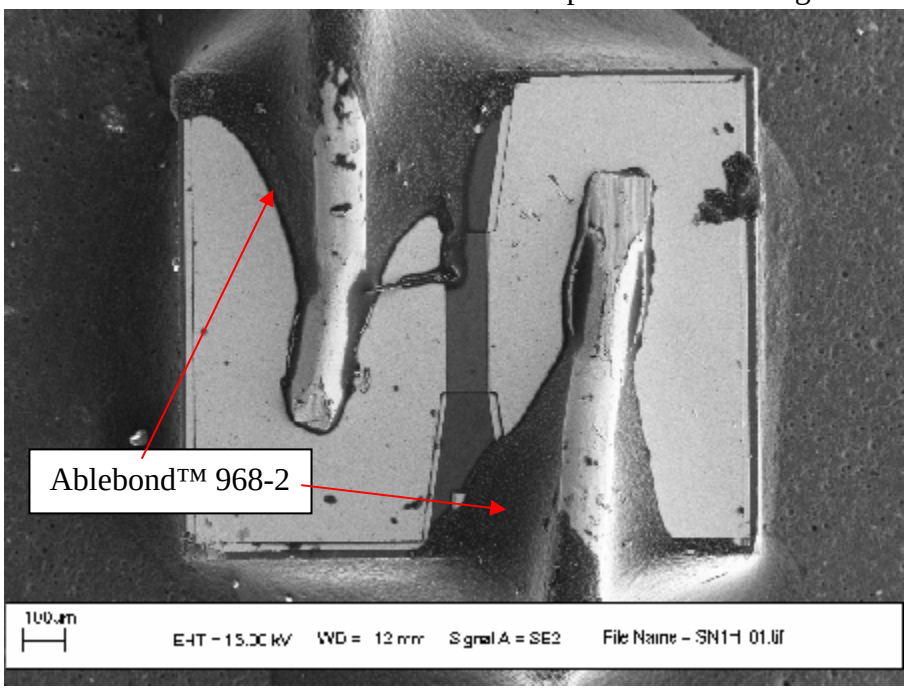

Figure 8. An example of the use of Ablebond™ 968-2 to support the wirebonds.

Another source of chloride could be the explosive CP used in the detonators or the

[2] In some cases resistance was higher than the specification limits of 1 ± 0.1 ohm, and corrosion was invariably found in these parts. It was not known, however, if the resistance for that part was high before thermal cycling. Corrosion was also found on parts that were within specification. Resistance values could point to corroded parts, but other causes exist for high resistance values, and resistance within specification does not guarantee a corrosion-free part.

pyrotechnic BCTK used in the igniters.[3] Both of these energetic materials contain perchlorate, but otherwise they are chemically different. The amount of chloride in CP is specified to be less than 100 ppm and is typically much lower than that.[4] The detonators were loaded with lot EL82936 in the initial pressing, and ion analysis of this lot did not detect any chloride ion present. The ion chromatography method used to analyze EL82936 can readily detect 10 ppm of chloride. The potassium perchlorate used in BCTK is a military specification material typically containing 100-200 ppm of chloride. BCTK is 29.5% potassium perchlorate by weight, and so the chloride content should be well below 100 ppm. A chloride analysis was not done nor is any required by specification.[5] Even though the chloride concentration of BCTK was thought to be low, BCTK was not ruled out as a source of chloride for corrosion in igniter headers.

The Material Safety Data Sheets (MSDSs) of all the chemicals used in wafer processing were also researched, and none of those chemicals contain chlorine as part of their structures. The MSDSs do not have information regarding the level of chloride contamination that may be present in those chemicals. Given the kinds of chemicals used and the cleaning that is part of the process, wafer processing was not thought to be a likely source of chlorine contamination. The community oven that was used to cure the adhesive was also mentioned as a possible source of chloride contamination, but this is easily corrected by using an oven that is dedicated to the manufacturing program.

In addition to chloride, moisture is necessary for aluminum corrosion products to form. Thus control of moisture is critical so that its presence does not provide a transport mechanism for chloride. According to anecdotal manufacturing history the local humidity was higher than usual during the time that both devices were built (aka “the rainy season”). The igniters were not dried during assembly, and additional precautions were not taken to minimize moisture exposure by storing parts in a desiccator, for example. The first 48 parts of the development lot detonators were loaded on a Friday and then stored in an oven at 140°F over the weekend until the parts could be welded together to seal the devices the following Monday. This temperature is not high enough to drive off water, and the lengthy time period and warmer than ambient temperatures may have been conducive to corrosion in susceptible parts.

For safety reasons, humidity was controlled to 40-60% when energetic materials were handled during manufacturing. CP is not known to be a hygroscopic material, and the water uptake at 98% humidity is 0.3% or less in 24 hours of exposure.[5] Since a relatively large quantity of the Ablebond™ adhesive was in direct contact with the lands, water uptake data were desired for this material also. None were available and so a screening study was done by placing pieces of cured Ablebond™ in controlled humidity environments and periodically recording the weight. The results are shown in Table 1. The amount of water actually involved in the corrosion reactions could not be determined, but the adhesive does not appear to absorb large amounts of water from its environment.

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[3] CP=2-(5-Cyano)tetrazolatopentaammine Cobalt (II) Perchlorate; BCTK = Boron Calcium Chromate Titanium Potassium Perchlorate

[4] The CP specification is SS339528, *Synthesis CP Explosive.*,

[5] The BCTK specification is SS1A5624, *Process Specification, boron/Calcium Chromate/Titanium/Potassium Perchlorate (BCTK) Mixture for the MC4779 Ignitor.*

Table 1. Moisture Uptake Study Results for Ablebond™ 986-2.

Sample ID	Weight change	Percentage change
Ablebond™ – 58% RH[1]		
Piece 330.43 mg	1.02 mg	0.31% in 5 weeks
Ablebond™ – 97% RH[2]		
Piece 180.96 mg	1.79 mg	1.0% in 5 weeks
Ablebond™ – Desiccator		
Piece 473.33 mg	(0.67 mg)	(0.14%) in 5 weeks

1 Saturated sodium bromide solution

2 Saturated potassium sulfate solution

Inspection and Analysis of Production and Fielded SCB Devices

The presence of corrosion in the developmental devices raised concern regarding corrosion in other SNL SCB devices. Some had recently been manufactured, but others had been in service for about ten years. The following samples were examined: 1) detonator headers with one Type 52 SCB per header and gold coated aluminum lands; 2) detonator headers with one Type 3-2 SCB per header and gold coated aluminum lands 3) detonators with one Type 52 SCB, aluminum lands (no gold coating), and loaded with the explosive CP; and 4) detonators that were manufactured about ten years ago with two Type 3-2 SCBs per header, gold coated aluminum lands, and loaded with CP. These dies were located in a specially machined area of the header rather than on the surface of the header as for Groups 1-3 as well as the developmental lots that had initiated this investigation.

Figure 9 shows an example of a detonator header from Group 1. Dies from approximately 20 headers that had previously been subjected to ESD testing were available for inspection and were examined for the presence of corrosion. No corrosion was found, but other issues were noted that could contribute to corrosion during the lifetime of the device such as contamination of the lands and manufacturing defects (discussed in the next section). The stains on the SCB shown in Figure 9 are typical of those that were found on the lands of some dies. FTIR analysis was attempted but only poor spectra could be obtained that indicated the possibility of a carboxylic acid salt. It could not be identified further—even after examination of the MSDSs of the die processing chemicals. Other spectra were consistent with human skin oil, but at least one stain was a well delineated rectangle located at

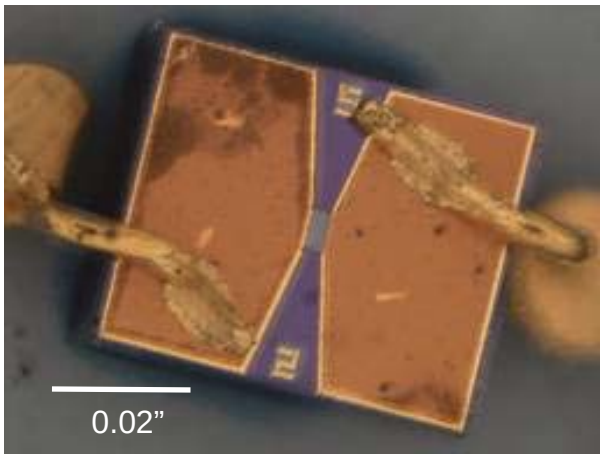


Figure 9. A Type 52 SCB that shows several areas of contamination.

the center of the die. One could speculate that a smear at the edge (such as shown in Figure 9) could be caused by handling the die/header without wearing gloves, but it is difficult to envision the scenario that would leave a well defined mark of skin oil in the center of a die. Perhaps the most likely scenario for contamination is the practice of using a community oven to cure parts after the application of Ablebond™. Notice that these wire bonds are not supported by adhesive.

Fifteen unloaded headers from Group 2 were obtained from production and were divided equally into three groups: 1) control headers; 2) headers that were cycled a total of 30 times;[6] and 3) headers that were cycled three times.[7] None of these headers showed evidence of corrosion either prior to or as a result of the thermal treatment.

Five detonators from Group 3 were thermally cycled a total of 30 times[5] and compared to five controls. None of these ten detonators showed any evidence of corrosion. An optical micrograph of one of the cycled headers after disassembly and powder removal is shown in Figure 10. Leak tests were also performed on these ten detonators to determine if moisture could be entering the device during thermal cycling. The leak rate was 4 x 10^{-9} std cc/sec for the control group, and 2 x 10^{-9} std cc/sec for the cycled group. These data show that all of the devices were hermetically sealed.

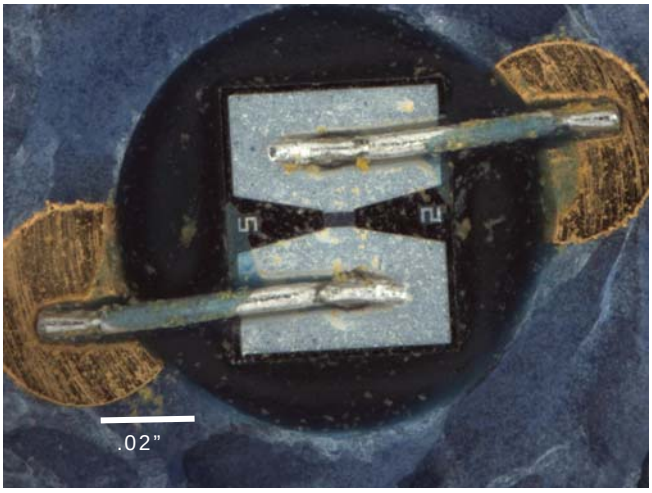


Figure 10. A Type 52 SCB with aluminum lands that had been thermally cycled 30 times.

In addition to these ten, four that had failed to function at -65°C and five that had been cycled four times[8] were examined. No evidence of corrosion was found on any of these units. All Group 3 detonators had been vacuum baked after the powder had been loaded and were then stored in desiccators until the closure disks were welded in place. It was also a process requirement to load and weld in the same day so that no in-process detonators were stored overnight.

[6] Five cycles between -54 C and 71 C and then 25 cycles between -40 C and 56 C.
[7] Three cycles between -40 C and 71 C with a two hour hold at each end of the temperature range.
[8] Four thermal cycles between -65°F (-54°C) and 165°F (74°C)

Finally a total of eleven detonators from Group 4 were examined. Two were controls, three had been through one set of thermal cycles, three through two sets of thermal cycles, and three through three sets of thermal cycles.[1] Each set involved thirty thermal cycles; thus, the three detonators in the last group were cycled ninety times. An optical micrograph of a die in the last group is shown in Figure 11. No evidence of corrosion was seen on any of the dies in any of the sets. A number of manufacturing defects were readily apparent and are discussed in the next section.

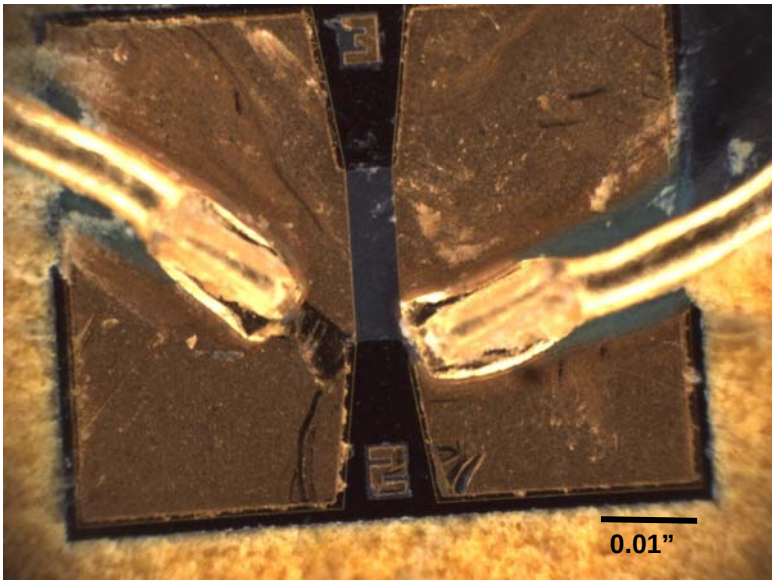
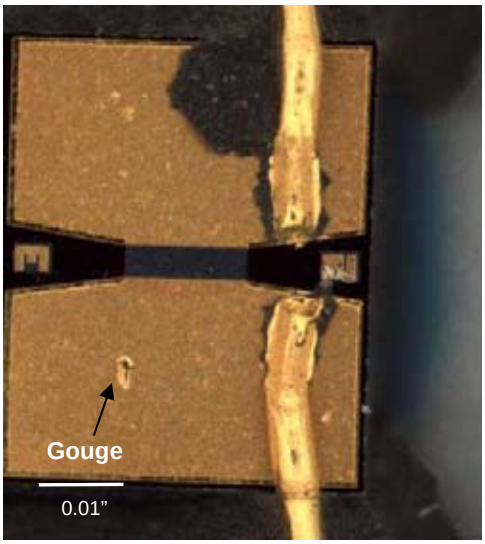


Figure 11. A Type 3-2 SCB with gold coated aluminum lands that had been manufactured about ten years ago and had been cycled a total of ninety times.

Observation of Manufacturing Defects

Observations of manufacturing defects have been made to different extents in all of the groups of SCB devices discussed thus far except for the Group 3 detonators with the aluminum lands that were not coated with gold. Because gold is a soft metal, it is easily deformed. After the gold layer is applied, the SCB bridge resistance is measured using a four point probe. Some amount of pressure must be applied to obtain a reading, but the operation tends to leave marks in the gold that sometimes go through to the aluminum layer. The probe appears to have a “snow plow” affect as shown in Figure 12. The gouges that were observed are probably caused during wire bonding when the die is being incorporated into a device header. Some of these go through to the polysilicon layer.



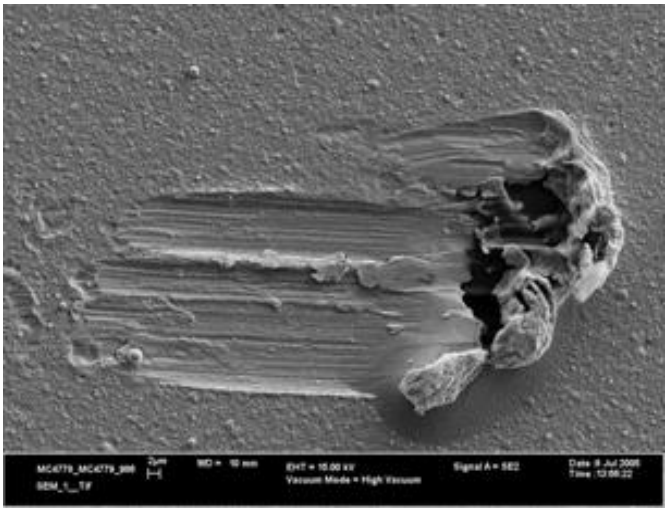


Figure 12. Optical and scanning electron micrographs of a mark left in the gold by application of a resistance probe.

In addition to breaches in the gold layer due to processes and tools, the gold layer in the recently fabricated dies appears to be somewhat porous. Figure 13 shows a scanning electron micrograph of the gold layer from a dual SCB. It looks as if the gold spheres are leaving craters which, in some cases, are deep enough to expose the aluminum layer. Figure 14 shows a scanning electron micrograph taken on a gold surface that was tilted and shows the columnar nature of the gold. The FIB cross section in Figure 15 shows several undesirable characteristics of the plated gold layer. The thickness of the layer is extremely variable. In the bottoms of the “craters”, the gold is extremely thin. It is likely that the layer is porous in the craters. In addition, a crack in the gold can be seen in the right crater. Again this suggests that the gold layer may, in fact, be porous. Neither craters nor spheres are observed in the gold lands of the devices made about ten years ago.

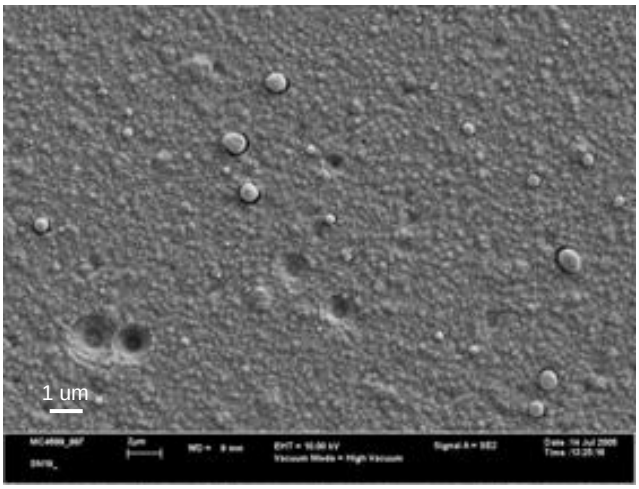


Figure 13. Scanning electron micrograph showing the surface of the gold layer on the SCB. Note the presence of “craters” (some of which contain spheres of gold) across the surface.

Once again in this investigation, the evidence is conflicting. Gold spheres typically form when the gold layer is deposited too quickly, but the records for the dual SCB wafer do not show a rapid rate, and if one looks closely at the scanning electron micrograph in Figure 12, one can see a sphere on top of the “snow plow” track. This can not be if the spheres resulted

from rapid deposition of gold because the resistance probe mark is only made after the deposition of the gold layer is finished.

Gold and aluminum form a galvanic couple in which aluminum is the anode and gold is the cathode. This process accelerates corrosion of aluminum. For galvanic corrosion to be active, both the anode and cathode must be exposed to the environment. In addition, an electrical connection between the anode and cathode is required. The gold-plated aluminum structure that is used in these SCB detonators provides an excellent example of galvanic coupling. In this case, if the gold layer is porous, it will actually enhance corrosion of an aluminum land rather than protect it as a solid layer of gold would.

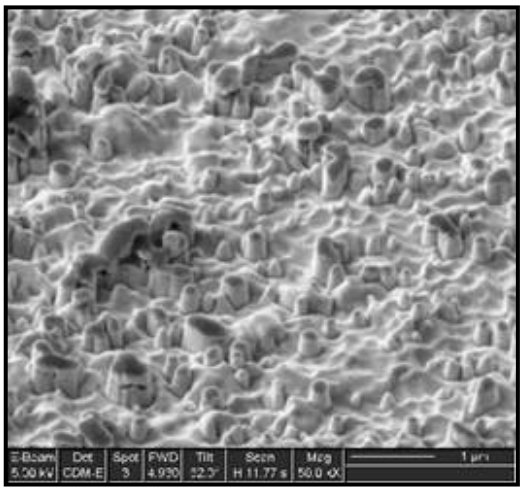


Figure 14. Scanning electron micrographs of the gold surface after tilting the sample at a small angle. Note the columns which contribute to excessive surface roughness.

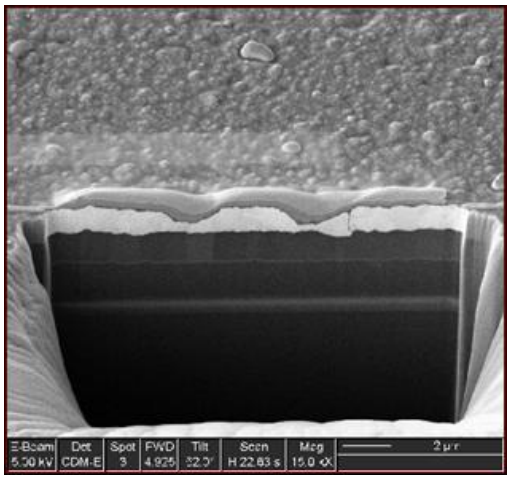


Figure 15. FIB cross sections of the gold plated land. Note the differences in gold thickness across the surface.

Atmospheric Corrosion Experiments

Igniter headers that had not been loaded with explosive and that showed no signs of corrosion were deliberately corroded by placing them in an atmospheric corrosion chamber containing chlorine and water vapor. Energy dispersive X-ray (EDS) analysis of the aluminum corrosion products showed that the element chlorine was present in all the samples that were examined. Measurements of bridge resistance were made continuously to follow the corrosion process (as corrosion proceeds, the resistance increases). The headers were removed from the chamber and examined when the resistance values were clearly out of specification.

Corrosion Tests with Gold-Plated Aluminum SCB Headers

Figure 16 shows resistance plots for three headers (six bridges) exposed to a humidity / chlorine environment. As can be seen, the resistance increases with exposure time, indicating that the device is undergoing corrosion. At the conclusion of the exposure, the samples were photographed (Figure 17). As can be seen, there is extensive attack of all of the structures. The attack is not uniform across the surface. Rather, it initiates at specific locations (where

defects in the gold layer expose the underlying aluminum) and spreads outwards from each initiation site. Corrosion products are visible across the surface of the device. The SEM image (lower right) shows that the corrosion sites (dark regions) are, in fact, isolated.

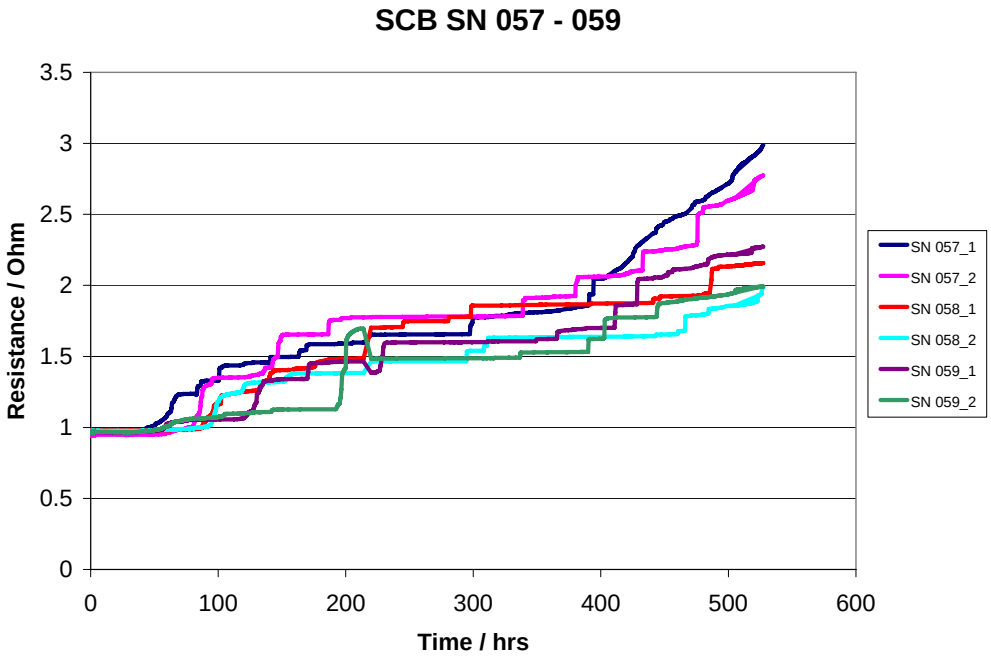


Figure 16. Resistance measurements for SCB headers exposed to 10 ppb chlorine gas (Cl_2) and 70% RH and 30C.

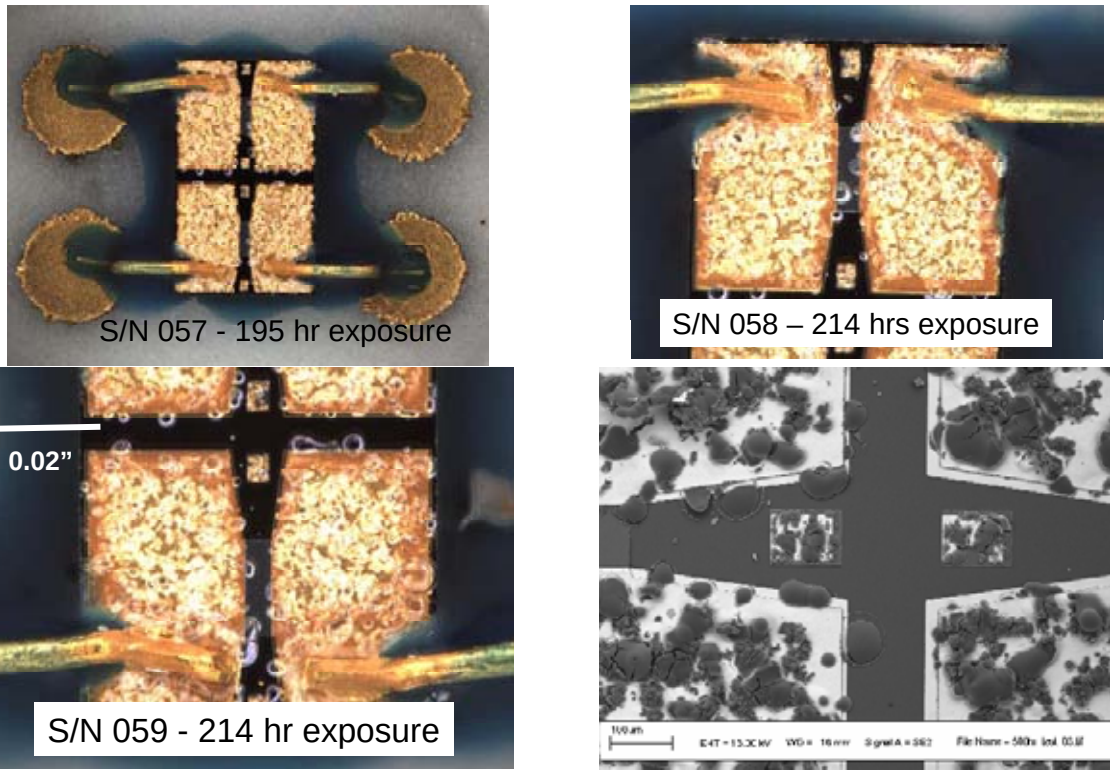


Figure 17. Optical and scanning electron micrographs of SCB headers exposed to 70% relative humidity and 10 ppb chlorine gas. The resistance plots are given in Figure 16.

These data are consistent with the observations of the previous section regarding porosity in the gold layer. Examination of the gold layer at high magnification also showed that rips and tears were present in the gold layer as shown in Figure 18. This is expected when the aluminum layer corrodes after the gold layer is deposited. Recall that earlier in this report the uniform thickness and lack of rips or tears in the gold layer were presented as evidence that the gold layer had been deposited after corrosion of the aluminum layer. The results of the corrosion experiments show that significant numbers of defects are present in the gold layer on these SCB igniter headers. Corrosion of aluminum was also observed at the edge of the lands. The gold layer is known to be thinner at the edges of the lands—in particular when the land is next to the bridge area.

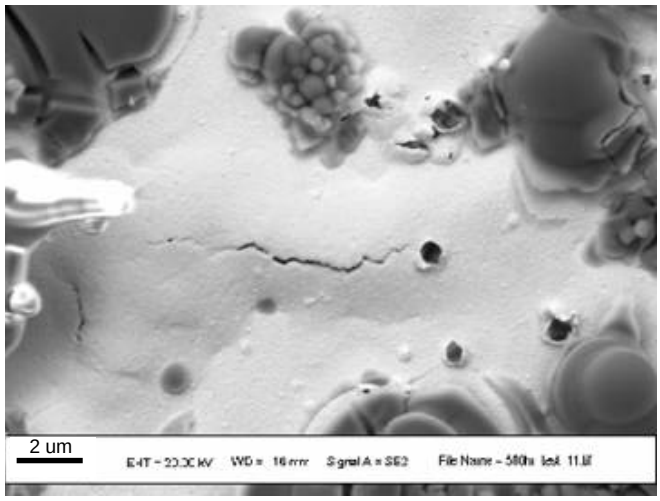


Figure 18. Scanning electron micrograph showing a rip in the gold layer due to expansion of the aluminum layer below as it corroded.

The resistance data and micrographs in Figure 19 and Figure 20 show the effect of chlorine concentration on the corrosion process. The data shown in Figure 19 were obtained after the concentration was reduced from 10 ppb to 2 ppb chlorine. The result is a substantial decrease in the rate of attack. In fact, the inset image shows limited attack of the surface, confirming the decrease in corrosion rate. The extent of attack is clearly less than that observed at 10 ppb chlorine (Figure 17). The data shown in Figure 20 are the result of a test run with only moisture (no chlorine). In this case, no increase in resistance was observed. The SCB surfaces show no evidence of attack. These results illustrate that exposure to humidity alone does not initiate corrosion. Notice that the wire bonds of these headers were liberally supported with Ablebond™ adhesive, and recall that Ablebond™ is suspected of being the most likely source of chloride. Perhaps the experimental conditions were not amenable to leaching chloride from the adhesive, or perhaps this particular lot of Ablebond™ did not contain as much chloride as the manufacturer's literature states. We do not know the lot to lot variability of Ablebond™ chloride content.

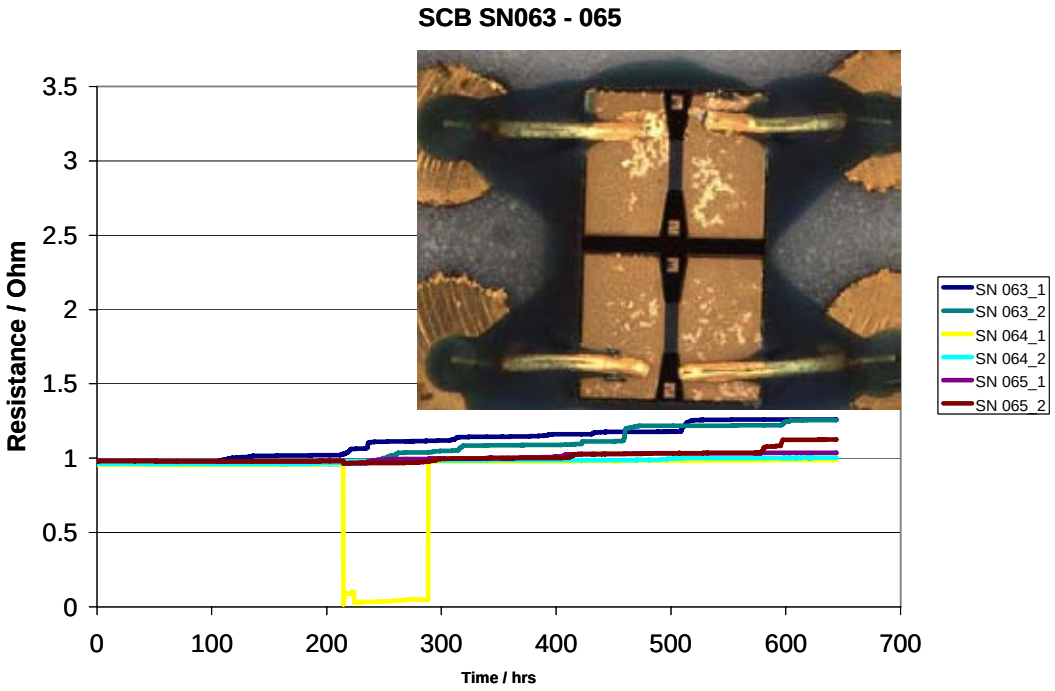


Figure 19. Resistance data for gold-plated SCBs that were exposed to 70% humidity and low concentrations (2 ppb) of chlorine. An optical image of one of the headers is inset. Note the lack of corrosion of the header.

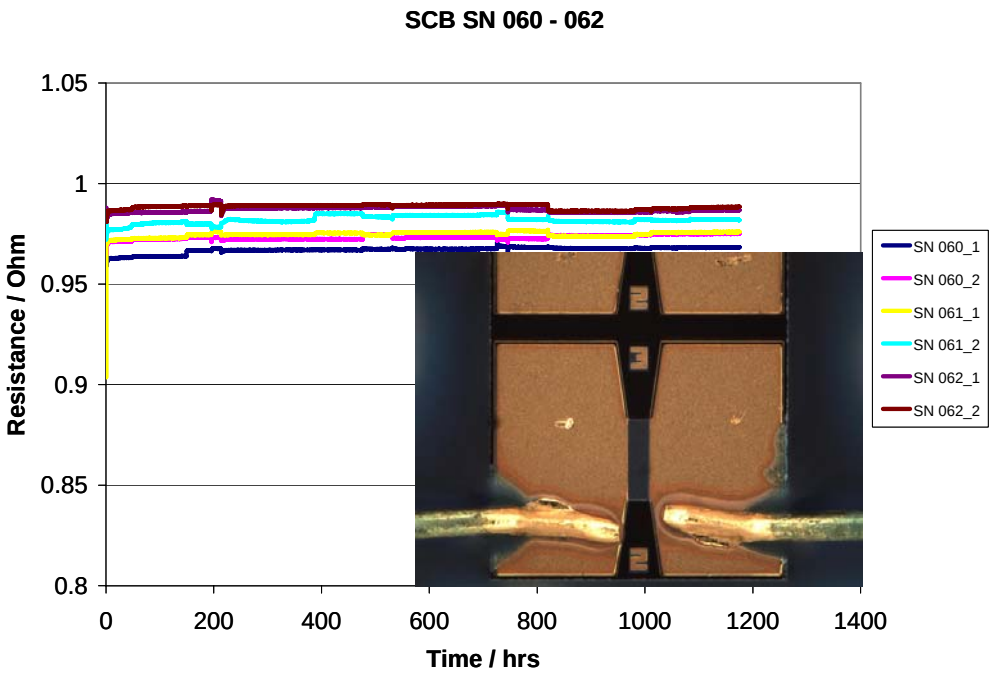


Figure 20. Resistance plot for SCB headers exposed to 70% humidity at 30 C with no chlorine.

Atmospheric Corrosion Tests with Aluminum SCB Headers

In the absence of the gold-aluminum galvanic couple, the rate of aluminum corrosion is expected to be slower. In order to test this, detonator headers with Type 52 aluminum SCBs (no gold layer) were subjected to environments containing various amounts of chlorine. The resistance results for 2 ppb Cl exposure are shown in Figure 21. In one of the more aggressive tests, the chlorine level was held at about 60 ppb (considerably more than for the gold-plated SCB devices shown previously). The humidity was 70%. There was no observed change in resistance throughout until more than 3000 hours of exposure. Optical images of the headers taken after 300 hours of test are shown in Figure 23. Note that there is no observable attack of either the aluminum land or the aluminum bond wire. The only area of attack was on the electrodes (posts) which are gold-plated iron-nickel. The corrosion is localized, presumably to defects in the gold plating. The color of the corrosion products is consistent with attack of an iron-based alloy. Thus, the conclusion is that the presence of gold on the lands significantly accelerates attack of the aluminum whenever defects in the gold are present.

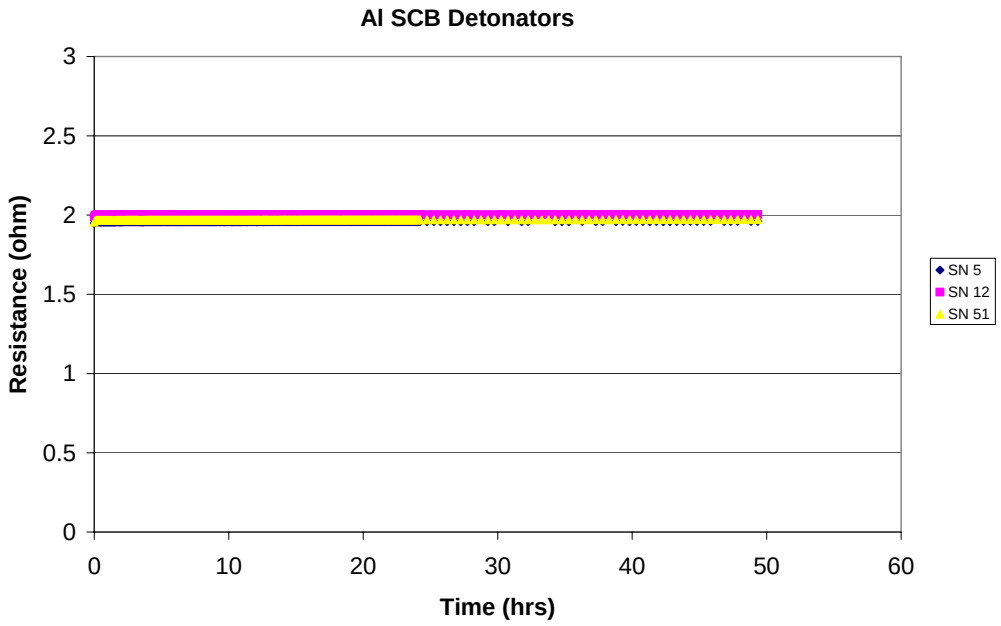


Figure 21. Resistance measurements from all aluminum SCB detonators exposed to low levels (2 ppb) of chlorine at 70% humidity and 30C.

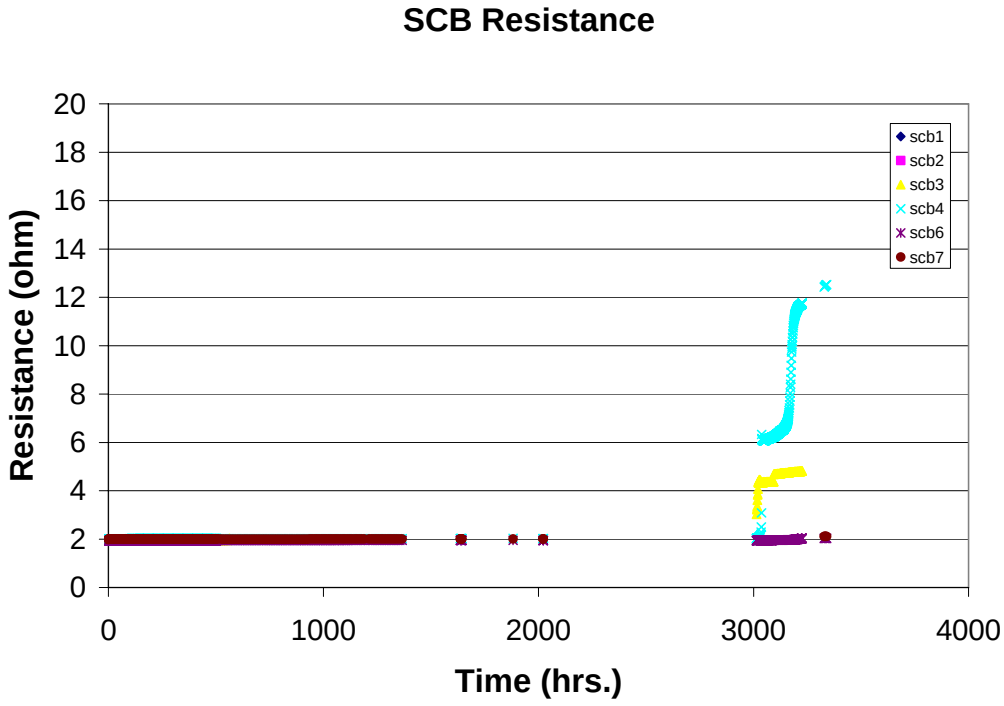


Figure 22. Resistance values for all aluminum SCB headers exposed to 60 ppb chlorine at 70% humidity.

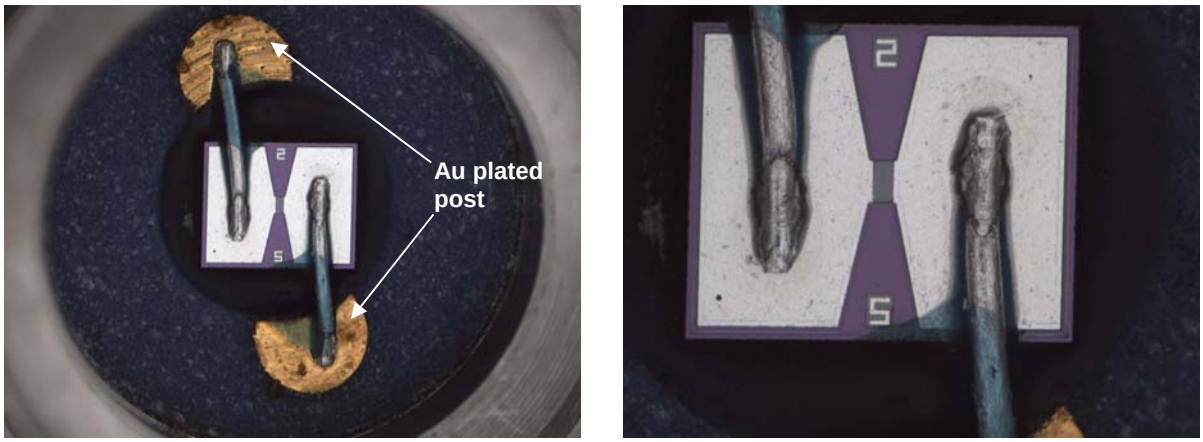


Figure 23. Optical images of all aluminum (no gold) SCB headers after exposure to humid chlorine environments. Note lack of attack of lands or bond wires. Some corrosion is seen on the gold-plated posts.

A second test was run with Type 52 all aluminum headers. The results are shown in Figure 24. These results are consistent with the previous test. At exposure times between 2500 and 3000 hours, an increase in resistance is beginning to be observed. Compare these results with those shown in Figure 16, where the resistance increases after about 100 hours of exposure at a chlorine level of 10 ppb. These results clearly demonstrate that the presence of a porous gold layer significantly accelerates the corrosion process.

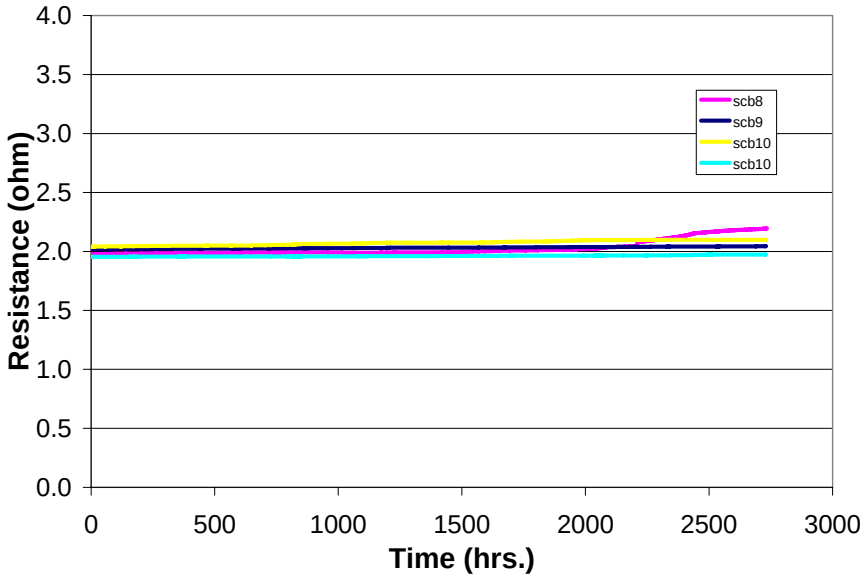


Figure 24. Resistance values for all aluminum SCB headers exposed to 60 ppb chlorine at 80% RH.

Lessons Learned For Subsequent Manufacture of SCB Devices

Even though not all questions could be answered thoroughly, several lessons learned from this investigation were successfully applied to the second development lot of detonators. First of

all, the gold layer was eliminated. The results of atmospheric corrosion experiments showed that corrosion products were formed at sites where the gold-aluminum galvanic couple was exposed. Thus eliminating the gold layer, removed possible corrosion sites due to porosity and cracks in the gold layer and marks left by the wire bonding tool and resistance probes. Also no corrosion was found upon examination of devices with all aluminum SCBs, and atmospheric corrosion experiments confirmed that even in the presence of moisture and chlorine, aluminum is more resistant to corrosion than the gold-aluminum galvanic couple. Secondly, Ablebond™ was not used to support the wires, and therefore it did not come into contact with the lands. The adhesive was only used to glue the die to the header. In this case the presence of chloride is not expected to be an issue if moisture is not present. Thirdly, the rigor in avoiding contamination and minimizing moisture was increased. All tooling and piece parts were cleaned and dried in a dedicated oven before use. Storage in dedicated desiccators was required for both the header assembly operations as well as the detonator assembly steps through the final laser weld, which hermetically seals the device. The energetic material, CP, was also dried, and % moisture was determined to confirm that the powder was dry. CP was also stored in dedicated desiccators. Parts were removed from the desiccators in batches. If the work was not completed before the next break, the parts were returned to the desiccators. Finally, inspection steps were added. All headers were inspected under 50 X with an optical microscope during header assembly and before they were loaded. Any with evidence of corrosion, stains, or marks were discarded.

Details of the manufacture and lot acceptance testing can be found in a separate report[9].

Summary

Corrosion of the aluminum layer of SCB dies was found on an occasional basis in developmental lots of a detonator and an igniter during a failure investigation. The aluminum layer was covered with a gold layer in both devices. When corrosion was present in the detonators, it was severe enough to delaminate the gold layer in many cases. In the igniters, the underlying aluminum corrosion gave the gold layer a rough appearance, but no delamination of the gold was seen. As it turned out, none of the failures could be attributed exclusively to corrosion, but the presence of corrosion is a concern in devices like these that require a long life.

Using scanning electron microscopy and focused ion beam cuts, evidence was gathered that showed the gold layer was deposited on aluminum that was already corroded because the gold layer intimately followed the contours of the aluminum and because the gold layer was of uniform thickness. Aluminum increases in volume as it corrodes, which would thin or tear an overlying gold layer. In some of the detonators, however, evidence showed that aluminum also corroded after the gold layer was deposited. Energy Dispersive X-Ray analyses of corroded areas showed that the element chlorine was present. A number of sources were considered including the explosive powders, wafer processing chemicals, and the oven used to cure the adhesive. The most likely source was the adhesive itself. The manufacturer's literature listed the chloride content at 215 ppm.

[9] "Design of Reliable CP-Based Semiconductor Bridge Detonators", Bill Tarbell & Tom Hafenrichter.

In addition to chloride, moisture is necessary for aluminum corrosion products to form. According to anecdotal manufacturing history, moisture was not rigorously excluded during the processing steps, and because these lots were developmental, records were not kept of all the processing steps. Also it was not possible to trace individual dies to a wafer in most cases. The design of the igniter die was unique, however, and only one wafer was made with this design. The corroded lands were easily observable with an optical microscope, and so over 1,000 dies from this wafer that had not been processed into igniter headers were inspected. No corrosion was found, which was surprising. If, indeed, gold was deposited onto corroded aluminum, and some of these dies were incorporated into headers, one would expect to have found some among the remaining dies.

It was also determined that thermal cycling, in and of itself, did not contribute to corrosion. Several devices representing two different types of SCBs (1 ohm and 2 ohm bridges) and SCB with and without a gold layer were cycled—some with explosive powder and some without. No cases were found where thermal cycling resulted in corrosion. Inspection of SCB devices manufactured recently and about ten years ago, however, did reveal defects such as marks and gouges in the gold layer that went through to the aluminum and sometimes the polysilicon layers, and porosity in the gold layer. The porosity appears to be recent and can be due to rapid deposition of the gold layer, but no changes in the processing that could account for this were found.

Gold and aluminum form a galvanic couple in which aluminum in the anode and gold is the cathode. The gold layer was added to protect the aluminum layer, but if the gold is porous, the galvanic couple is exposed in numerous places with the result that the presence of the gold could actually enhance aluminum corrosion rather than protect it. Atmospheric corrosion experiments were conducted with unloaded and uncorroded igniter headers that had a porous gold layer in the SCBs. These headers were exposed to chlorine at high humidity, and the resistance values of the bridges were collected over time. The experiment was stopped when the resistance values were clearly out of specification. Optical and scanning micrographs of the SCBs showed extensive corrosion that originated at distinct points on the surface of the gold. Buckling and tearing of the gold layer was also observed. Experiments were repeated with lower levels of chlorine, and, as expected, lower chlorine levels correlated with decreased corrosion and smaller changes in the resistance values.

Atmospheric corrosion studies were also performed with all aluminum SCBs. Exposure to high humidity and higher levels of chlorine than were used with the gold/aluminum SCBs resulted in no visible corrosion of the aluminum lands when examined by optical microscopy. This was true at times long after the resistance values of the gold/aluminum SCBs started to rise, indicating the start of corrosion reactions.

Even though not all of the questions could be thoroughly researched and answered, several lessons learned from this investigation were applied to a second lot of developmental detonators. The gold layer was eliminated which eliminated concerns about its porosity, gouges, and other marks. Ablebond™ was only used to bond the die to the header and was not used to support the wirebonds. Even though the adhesive could contain high levels of

chloride, it was not in close proximity to the lands and bridges of the SCB. The rigor of minimizing moisture levels was increased by using drying steps, desiccated storage, and limited processing time. Inspection steps were also added to eliminate any SCBs with corrosion, stains, or marks to avoid initiation of reactions with age. These steps led to a successful manufacture of the second lot of developmental detonators, with no evidence of corrosion.

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